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PROPERTIES OF CP: COEFFICIENT OF THERMAL EXPANSION, DECOMPOSITION KINETICS, AND REACTION TO SPARK, FRICTION AND IMPACT

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October 12, 2005

Propellants, Explosives, Pyrotechnics

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PROPERTIES OF CP: COEFFICIENT OF THERMAL EXPANSION, DECOMPOSITION KINETICS, AND REACTION TO SPARK, FRICTION AND IMPACT

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Abstract
The properties of pentaamine (5-cyano-2H-tetrazolato-N2) cobalt (III) perchlorate (CP), which was first synthesized in 1968, continues to be of interest for predicting behavior in handling, shipping, aging, and thermal cook-off situations. We report coefficient of thermal expansion (CTE) values over four specific temperature ranges, decomposition kinetics using linear and isothermal heating, and the reaction to three different types of stimuli: impact, spark, and friction. The CTE was measured using a Thermal Mechanical Analyzer (TMA) for samples that were uniaxially compressed at 10,000 psi and analyzed over a dynamic temperature range of -20˚C to 70˚C. Differential scanning calorimetry, DSC, was used to monitor CP decomposition at linear heating rates of 1-7 ˚C min^{-1} in perforated pans and of 0.1-1.0 ˚C min^{-1} in sealed pans. The kinetic triplet was calculated using the LLNL code *Kinetics05,* and predictions for 210 and 240 ˚C are compared to isothermal thermogravimetric analysis (TGA) experiments. Values are also reported for spark, friction, and impact sensitivity.

Keywords: TMA, CTE, high explosive, energetic materials, CP

INTRODUCTION

The high explosive CP was first synthesized in 1968 by Unidynamics, Inc., Phoenix, Arizona [1]. This was a successful collaboration between Unidynamics and Sandia National Laboratories, Albuquerque, New Mexico, to develop a detonator that employed an energetic coordination compound. In 1977 the first production of CP began and by 1979 the first production of a CP detonator for DOE had been successfully accomplished.

Some 36 years later, scientists are still exploring by use of thermal properties and chemical degradation of CP and other energetic materials to understand properties that affect the use, safe handling, and functional lifetime of the material. Textbook and literature values of various material properties are useful but are often given as singular values at ambient

temperatures and pressures. Such information does not always suffice for situations such as thermal cook-off where a dynamic temperature-pressure range is involved [2,3].

This study was conducted to provide data on CP, lot # EL-82936, and to compare the observations to previously analyzed lots of CP. Here we report the coefficient of thermal expansion, CTE, of pressed material and the decomposition kinetics calculated from linear heating rates in perforated and sealed pans. In addition, we report various types of initiation sensitivity tests: drop hammer, spark and friction.

Table 1: Properties of CP [4,5]

Molecular weight	436.98 g mol^{-1}
Color	Yellow
Crystal structure	Monoclinic
Crystal density	1.974 g cm^{-3} x-ray diffraction
Coefficient of thermal expansion, CTE	60×10^{-6} m m^{-1} K^{-1} (298 to 323 K)
Heat capacity	C_p(cal/g˚K) = 0.646 (353-453 K)
Electrostatic sensitivity	Greater than 20kV at 600pF and 500Ω on loose powder and unconfined pellet

METHODS AND RESULTS

Sample

The CP sample material for this study (lot # EL-82936) was manufactured by Pacific Scientific of Chandler, AZ.

Coefficient of Thermal Expansion

Thermomechanical analysis (TMA) measures linear or volumetric changes as a function of time, temperature and force [6]. It can provide a better understanding of physical properties such as glass and solid-solid phase transitions. Most analyses are presented in the form of the coefficient of thermal expansion:

$$dL/(dT * L_o) = \text{CTE (coefficient of thermal expansion)} \quad (1)$$

where dL is the change in length (μm), dT is the change in temperature (˚C), and L_o is the initial length (m).

We measured the CTE of CP using a TA Instruments Model 2940 TMA that was controlled by a TA 500 Thermal Analyzer. A TMA Mechanical Cooling Accessory, manufactured by TA Instruments, controlled the temperature. A quartz micro-expansion probe was used for all samples with a force of 0.01 Newtons (N). Ultra high purity nitrogen carrier gas was used at a constant flow rate of 100 cm^3 min^{-1}. Samples were heated at a linear heating rate of 3 ˚C min^{-1}.

Temperature, force, probe and cell constant calibrations were carried out as prescribed [7], using indium, lead, tin and zinc metals along with aluminum standard reference material. Coefficient of thermal expansion measurements using a certified aluminum standard had less than ± 2 % errors associated over the temperature range of –20 to 65˚C.

Our CP sample was uniaxially pressed at room temperature in a compaction die using a single pressing cycle of 10,000 psi. Table 2 gives the measured sample mass, volume, density and dimensions used for this experiment. Comparison to the theoretical maximum density (TMD) [8] indicated the sample achieved 85.7% TMD.

Figure 1 shows a plot of dimensional change versus temperature. CTE values were calculated using equation 1 and are listed in Table 3 for six specific temperature intervals. The errors associated with this experiment range from 2-16 parts in 100.

Table 2: Sample mass, volume, density and dimensions

Material	length, cm	diameter, cm	mass, g	volume, cm^3	density, g cm^{-3}
CP	0.089	0.508	0.306	0.0180	1.696

Table 3: CP CTE values, μm m^{-1} ˚C^{-1}

Material	-20˚C to 0˚C	0˚C to 25˚C	25˚C to 50˚C	50˚C to 75˚C	75˚C to 100˚C	100˚C to 125˚C
This work	59	55	59	56	55	62
Lit. value [9]	58	59	60	62	66	71

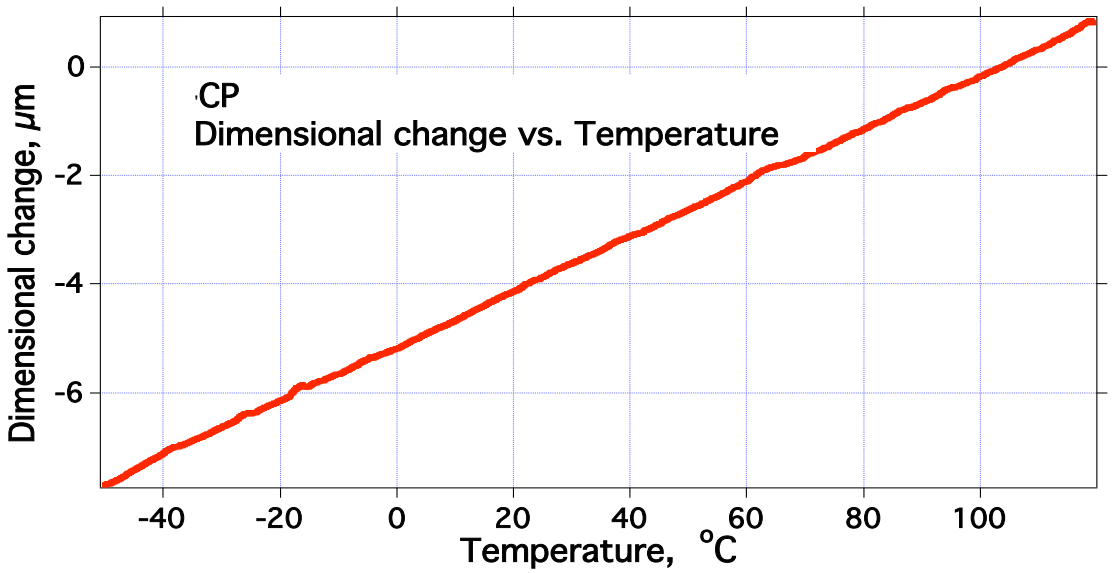

Figure 1. CP Dimensional change versus temperature.

Decomposition kinetics

We measured thermal decomposition kinetics using differential scanning calorimetry (DSC) and simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA). DSC analyses of CP were carried out using a TA Instruments Model 2920 and a purge flow of 50 cm^3/min of ultra-high-purity nitrogen. Two types of pans were used: Perkin-Elmer aluminum pans with a small pin-sized perforation to allow generated gases to escape during decomposition, and TA instruments hermetically sealed aluminum pans. Samples sizes were limited to prevent bursting the pan. Heating rates of 1.0, 3.1, and 7.2 ˚C min^{-1} and sample sizes <0.2 mg were used in the perforated pans; heating rates of 0.1, 35, and 1.0 ˚C min^{-1} and samples sizes of ~0.45 mg were used in the hermetically sealed pans. TGA and DTA analyses used a TA Instruments Simultaneous Differential Thermogravimetric Analyzer (SDT), model 2960, and TA open aluminum pans. Degradation was carried out under nitrogen carrier gas at a flow rate of 100 cm^3/min. Data was analyzed using the LLNL kinetics analysis program *Kinetics05*.

Chemical kinetic analysis is full of pitfalls for complex reactions. The basic starting equation gives the rate of reaction in terms of a rate constant times a function of the extent of reaction:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \qquad (2)$$

where the temperature dependence of k is typically described by an Arrhenius law ($k=A\exp(-E/RT)$), where A is a frequency factor, E is an activation energy, and R is the gas constant, α is the fraction converted, and f is a function that depends on mechanism.

One of the simplest, yet generally reliable, methods of kinetic analysis is Kissinger's method [10], in which the shift of temperature of maximum reaction rate (T_{max}) with heating rate (β) is given by

$$\ln(\beta/T_{max}^2) = - E/RT_{max} + \ln(AR/E). \quad (3)$$

The CP reaction rate profile has a very sharp peak, and this method yielded $A=3.13\times10^{14}$ s^{-1} and $E=179.2$ kJ mol^{-1}, with a standard error of 8.2 kJ mol^{-1} on the activation energy, for DSC data in perforated pans.

The reaction profile width is only 18% of the peak width of a first-order reaction, indicating some type of autocatalytic or shrinking core mechanism. In addition, the reaction has leading and trailing shoulders, indicating multiple processes. An increasingly common approach for analyzing such a complex reaction profile is some type of isoconversional method; we use Friedman's method here, in which an effective 1st-order k is determined at each percent of conversion by dividing the measured rate by the fraction converted and fitting the resulting rate constant at extent of conversion to an Arrhenius law [11]. The result is a measure of A and E as a function of conversion, as shown in Figure 2 for our CP data.

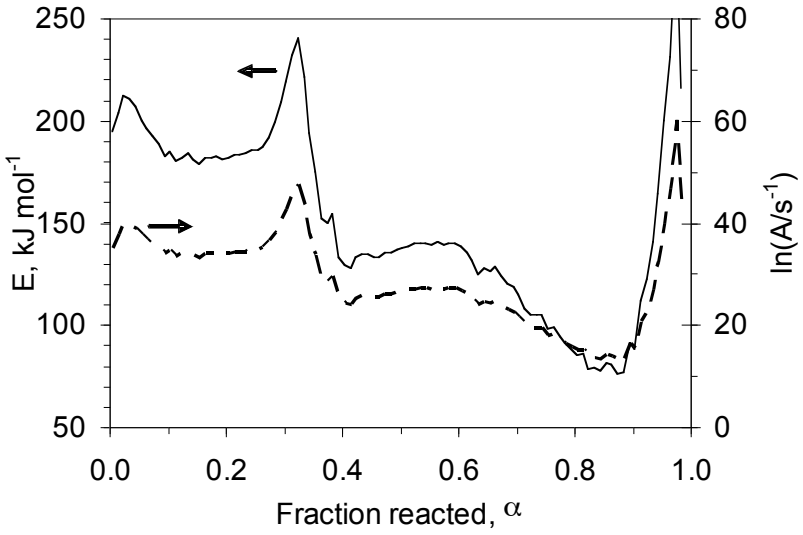

Figure 2: Conversion dependence of A and E determined by Friedman's method.

A comparison of measured and calculated reaction rates is shown in Figure 3. Sensitivity to baseline selection in combination with the extremely sharp reaction profile causes some minor problems with the method. However, the shift in reaction profile is only about 1 °C, which corresponds to a change in *A* by a factor of 8.5%. A similar isoconversional analysis by B. Roduit of AKTS yielded very similar *A* and *E* parameters up through 90% conversion, but both *A* and *E* then plunged towards zero above 90% conversion. The AKTS software has baseline optimization and profile shifting features, which introduce a difference from our analysis for this region of the reaction. The difference has little practical effect, however, since the material is nearly spent by that point.

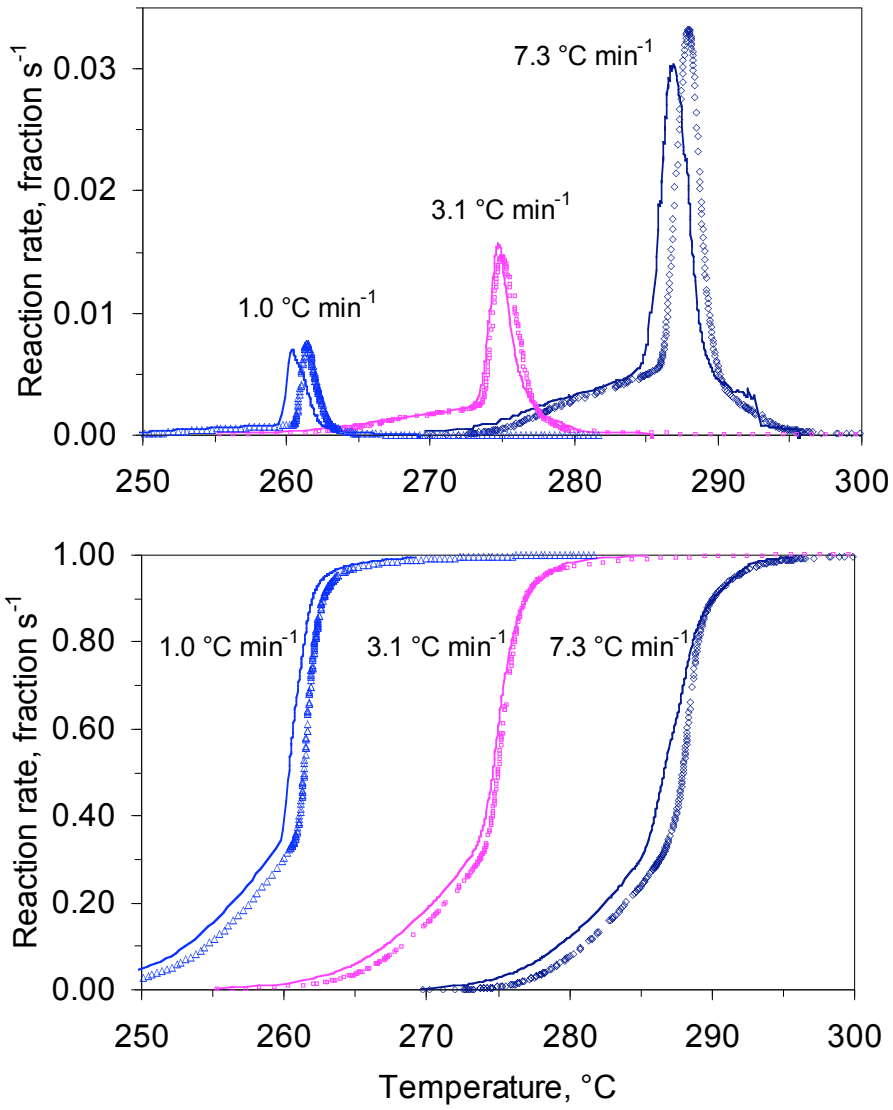

Figure 3: Comparison of measured and calculated reaction rates and fractions reacted for Friedman's method.

The reaction rate as a function of heating rate for hermetically sealed pans is shown in Figure 4. The fastest heating rate here is the same as the slowest heating rate in Figure 3, so the reaction profile is shifted up in temperature by about 40 ˚C (261 to 310 ˚C). This corresponds to a slowing of the reaction rate by a factor of about 35, assuming an *E* of 180 kJ mol^{-1}. The Kissinger parameters for the sealed pan runs are 5.70×10^{14} s^{-1} and 186.7 kJ mol^{-1}, which suggests that most of the retardation is due to a slight increase in activation energy. Friedman parameters were not determined due to the variability of the reaction profile at different heating rates. One could use the Friedman parameters in Figure 2 with *A* decreased by 35×.

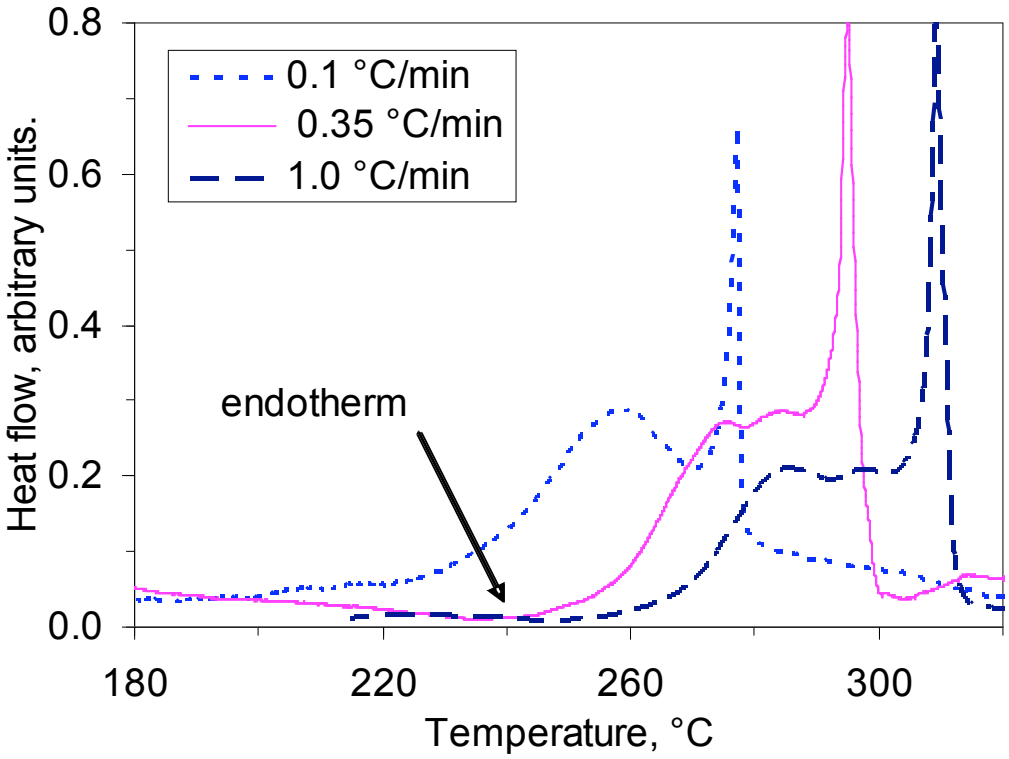

Figure 4: Decomposition rate of CP in sealed pans as measured by heat flow in a DSC apparatus.

Simultaneous TGA and DTA decomposition rates were also measured at constant temperature. Results at 210 and 240 ˚C are shown in Figure 5. The sample was heated to the final temperature over 20 min. Minor mass loss occurred at ~100 ˚C during heatup. After reaching the final temperature, the rate of mass loss gradually accelerated until it increased rapidly with an accompanying spike in the DTA signal.

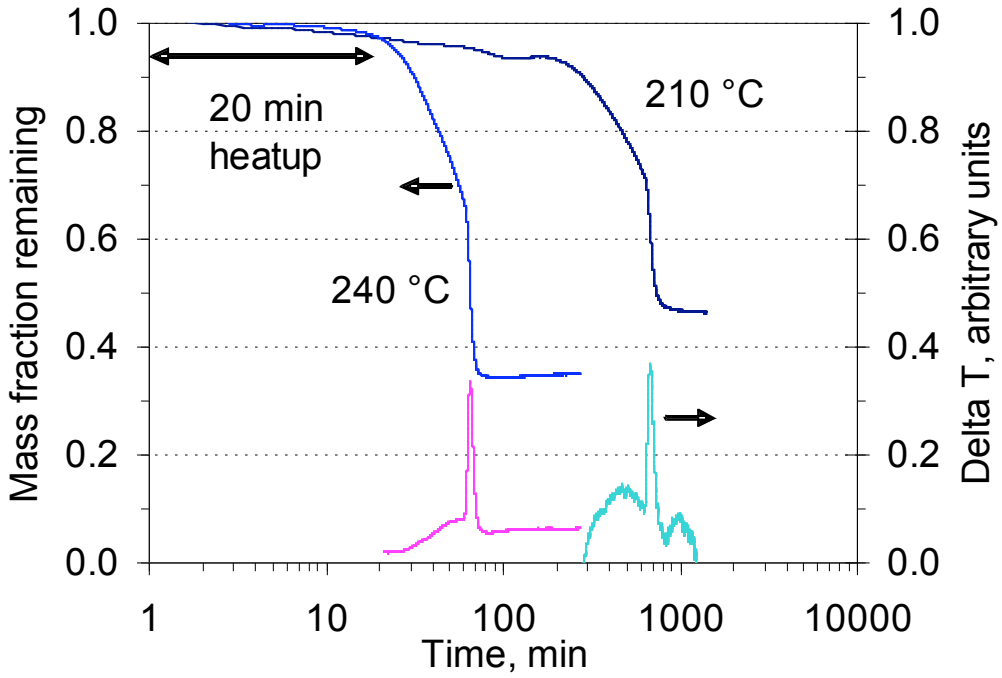

Figure 5. Fraction of mass remaining and rate of heat released as a function of time for CP heated to 210 and 240 ˚C.

An interesting challenge to any kinetic model is its ability to match results for experiments outside the range of the calibration set. Such a test is shown in Figure 6, in which the Friedman parameters are used to predict isothermal rates. The model works quite well, predicting both the general shape of the reaction profile and the time of rapid exotherm. The gradual increase in mass loss at 210 ˚C up to 100 min. may be instrumental drift, in which case the agreement would be even better.

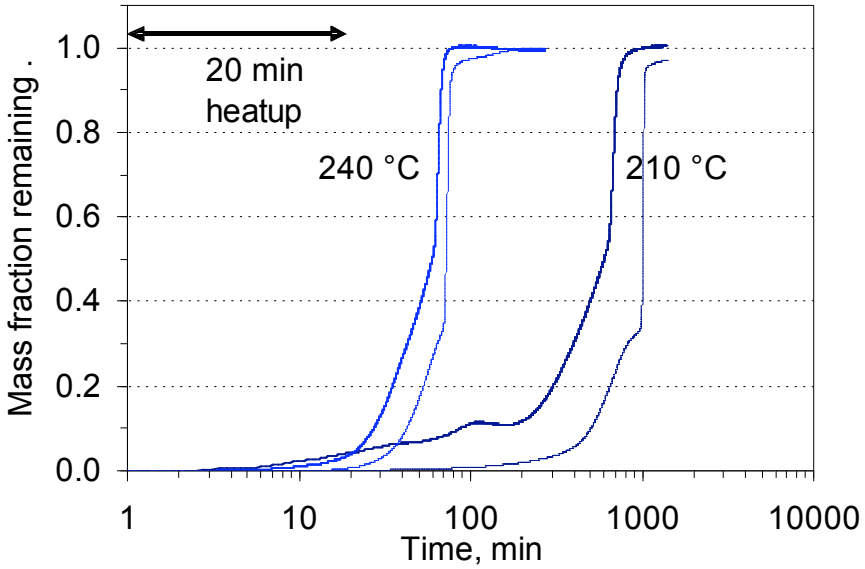

Figure 6: Comparison of measured (solid lines) and predicted (dashed lines) mass loss at constant temperature. The prediction used an isoconversional model (dashed line) that was calibrated at constant heating rates.

Reaction to various stimuli

Small scale testing of energetic materials and other compounds is done to determine sensitivity to various stimuli, including friction, impact and static spark. These tests are of monumental importance for several reasons, but mainly to establish parameters for the safety in handling and carrying out experiments that will describe behavior of materials that are commonly stored for long periods of time. This report will include the existing tests often referred to as drop hammer (impact sensitivity), friction, and spark. The accumulated data is then discussed.

Friction sensitivity

The frictional sensitivity of CP was evaluated using a B.A.M. high friction sensitivity tester, shown in Figure 7. The tester employs a fixed porcelain pin and a movable porcelain plate that executes a reciprocating motion. Weight affixed to a torsion arm allows for a variation in applied force between 0.5 and 36.0 kg, and our tests used a contact area of 0.031 cm^2. The relative measure of the frictional sensitivity of a material is based upon the largest pin load at which less than two ignitions (events) occur in ten trials. No reaction is called a "no-go", while an observed reaction is called a "go." CP was observed to have 1/10 "goes" at 1.0 kg at 68˚F and a relative humidity of 60%. CP was compared to an RDX calibration sample, which was also found to have 1 event in 10 trials at 12.4 kg. CP is considered to be friction sensitive.

Figure 7: B.A.M. high-friction sensitivity tester.

Spark sensitivity

The sensitivity of CP toward electrostatic discharge was measured on a modified Electrical Instrument Services Electrostatic Discharge (ESD) Tester, which is shown in Figure 8. Samples were loaded into Teflon washers and covered with a 1-mm thick Mylar tape. The density of this packed material was 1.4 cm^3 g^{-1}. The ESD threshold is defined as the highest energy setting at which a reaction occurs for a 1 in 10 series of attempts when discharged through 510 Ω. Tests were run on powder and pellets at 68˚F and a relative humidity of 56%. No reactions were observed (0/10) at 10 kV (1J). This material is not spark sensitive under these specific conditions.

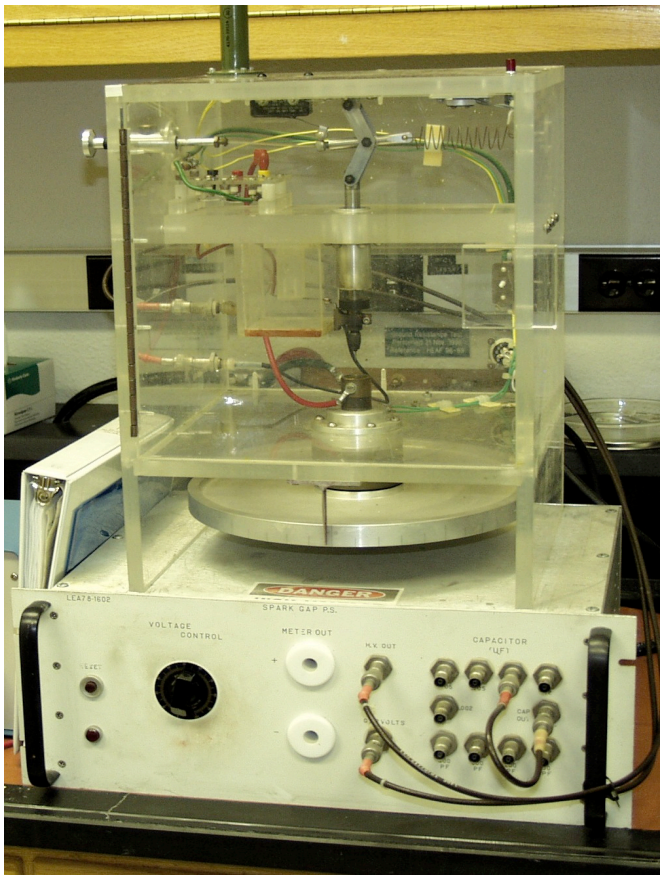

Figure 8: Electrical Instrument Services Electrostatic Discharge (ESD) Tester.

Impact sensitivity (drop hammer)

An Explosives Research Laboratory Type 12-Drop Weight apparatus, more commonly called a "Drop-Hammer Machine" was used to determine the impact sensitivity of CP relative to the primary calibration materials PETN, RDX, and Comp B-3 at 68˚F and 56% relative humidity. The apparatus, shown in Figure 9, was equipped with a Type 12A tool and a 2.5-kg weight. The 35-mg ± 2-mg powder sample was impacted on a Carborundum "fine" (120-grit) flint paper. A "go" was defined as a microphone response of 1.3 V or more as measured by a model 415B Digital Peakmeter. A sample population of 15 was used. The mean height for "go" events, called the "50% Impact Height" or Dh_{50}, was determined using the Bruceton up-down method. The Dh_{50} for CP for this experiment was 60.6 ± 1.0 cm. For comparison, the Dh_{50} of PETN, RDX, and Comp B-3 were measured at 15.5, 34.5, and 41.4 cm, respectively.

Figure 9: Explosives Research Laboratory Type 12-Drop Weight apparatus.

DISCUSSION

Our CP thermal expansion values as a function of temperature agree with the only previous report known to us [9]. The comparison of CP, PETN, HMX and RDX in Table 4 shows that CP's CTE values are basically constant over the temperature range of -25˚C to 75˚C. CP's values are the lowest of this set of energetic materials except at -25˚C where HMX is approximately 39% less. PETN's CTE starts approximately 40% higher than CP, and its CTE increases approximately 11% over the temperature range. HMX and RDX molecular structures are well known and have been studied extensively in the past. Both HMX and RDX CTE's almost double over the dynamic temperature range of -25˚C to 75˚C.

Table 4: CTE values (μm m^{-1} $˚C^{-1}$) for CP, PETN, HMX and RDX.

Temperature, ˚C	CP	PETN	HMX	RDX
-25	57	82	35	49
25	57	88	49	65
75	56	91	82	96

Searcy and Shanahan [13] report that decomposition of CP occurs as a three-step mechanism where step 1 is the dissociation of the ammonia ligand, and is an endothermic process. Step 2 is the oxidation of the ligand around the cobalt atom by the perchlorate ion. Step 3 is the oxidation of the residual solid products by the perchlorate ion. This reaction sequence accounts for the complex reaction profile we observe. The third step is very rapid, as is indicated by the sharp reaction peak in Figs. 3-5. In additional thermogravimetric experiments at 20 ˚C min^{-1}, using a few tenths of mg, we reproducibly observed a weight "gain" from the explosive impulse followed by complete mass loss over a 15 s interval. The first step appears to accelerate HMX decomposition in CP-HMX mixtures [14].

Two reaction characteristics of interest are the peak reaction temperature for a given heating rate and the activation energy, which describes how it shifts with a change in heating rate. Massis et al. [11] report that sealed samples decompose about 50 ˚C higher in temperature compared to open samples. The decomposition temperatures reported here for pierced pans and sealed pans, respectively, agree well with those reported by Massis et al. when differences in heating rate are taken into account.

Using Kissinger's method [9], Massis et al. [11] report a range of activation energies from 164 to 208 kJ mol^{-1} based on the concentration of an impurity that is described as an amide complex (Table 5). Our perforated and sealed pan results of 179.5 and 186.7 kJ mol^{-1}, respectively, fall near the middle of that range. Massis et al. contend that varying amounts of an amide complex impurity causes the activation energy to shift; one can thereby estimate the stability. However, there are no clear trends in the activation energy as a function of amide complex content, and we did not do an impurity analysis on our material, so we can merely say that our results for lot 82936 lie within the range of literature values. They also observe that gaseous decomposition products such as ammonia appear to inhibit the decomposition by shifting the reaction to higher temperatures.

The methods and apparatus used for drop hammer, spark and friction tests described here so that other experimenters can compare our results to others with reference to these procedures. Listed below in Table 6 are reported literature values and values observed in this work that clearly reflect the differences in testing apparatus.

Table 5: Activation energy (kJ mol^{-1}) of CP with varying amounts of amide complex impurity. Experiments are nonisothermal unless otherwise noted.

Sample configuration	Lot 36353A [10] 0.9 – 1.0 %	Lot 47344 ~ 4 %	Lot 36164 8 – 10 %	Lot 82936 Amide complex % unknown
Open [11]	186	208	164	---
Open (iso) [11]	182	179	174	---
Perforated pan (this work)	---	---	---	179.5
Hermetic pan [11]	144	183	176	---
Hermetic pan (this work)]	---	---	---	186.7

Table 6: Summary of safety test results

Test	CP, literature [15]	This work
Friction (fine)	30 psig @ 8ft s^{-1} 180 psig @ 3ft s^{-1}	455 psig @ 0.1 ft s^{-1}
Friction (coarse)	< 30 psig @ 8ft s^{-1} 420 psig @ 3ft s^{-1}	------
ESD threshold (J)	[a] 0.165 (fine) 0.326 (coarse)	> 1.0 @ 510Ω
Dh_{50} (cm)	19 (fine) 9 (coarse)	61
E (kJ mol^{-1})	164-208	179.5, 186.7

[a]: Samples were approximately 35 mg in mass; no density or sample dimensions are available.

It is difficult to say whether our CP sample is more or less sensitive to friction because of the difference in drag rate. The ignition pressure obviously increases with a decrease in velocity in the Indian Head data, but two points is insufficient to define a relationship. One might presume that ignition occurs at a threshold temperature rise that is a function exposure time according to an Arrhenius realationship. Frictional temperature rise should be proportional to the rate of energy input, hence force times velocity, since the rate of energy dissipation is also proportional to ΔT. However, the exposure time is inversely proportional to velocity. More information at multiple drag velocities is needed to sort this out.

Our drop hammer height is higher (lower sensitivity). This could be because our sample is finer by comparison to their particle-size trend. Overturf [16] reports that our sample has a specific surface area of 0.573 $m^2 g^{-1} \pm 0.02 m^2 g^{-1}$, but there is no surface area reported for the Indian Head samples. Indian Head report particle sizes of 70-90 μm for the fine powder and 100-200 μm for the coarse powder, which results in smaller calculated surface areas. Using a Zeiss microscope we measured CP particles in the 5-20 μm range (see Figure 10), which confirms that our powder is finer than either Indian Head powder.

Our ESD threshold is higher (less sensitive) even though our particle size is smaller, which should cause the threshold to decrease [16]. This may be due to the electrical pulse that is delivered to the sample. Ours is discharged through a resistance of 510 Ω to mimic the resistance of the human body, but we do not know the resistance used at Indian Head.

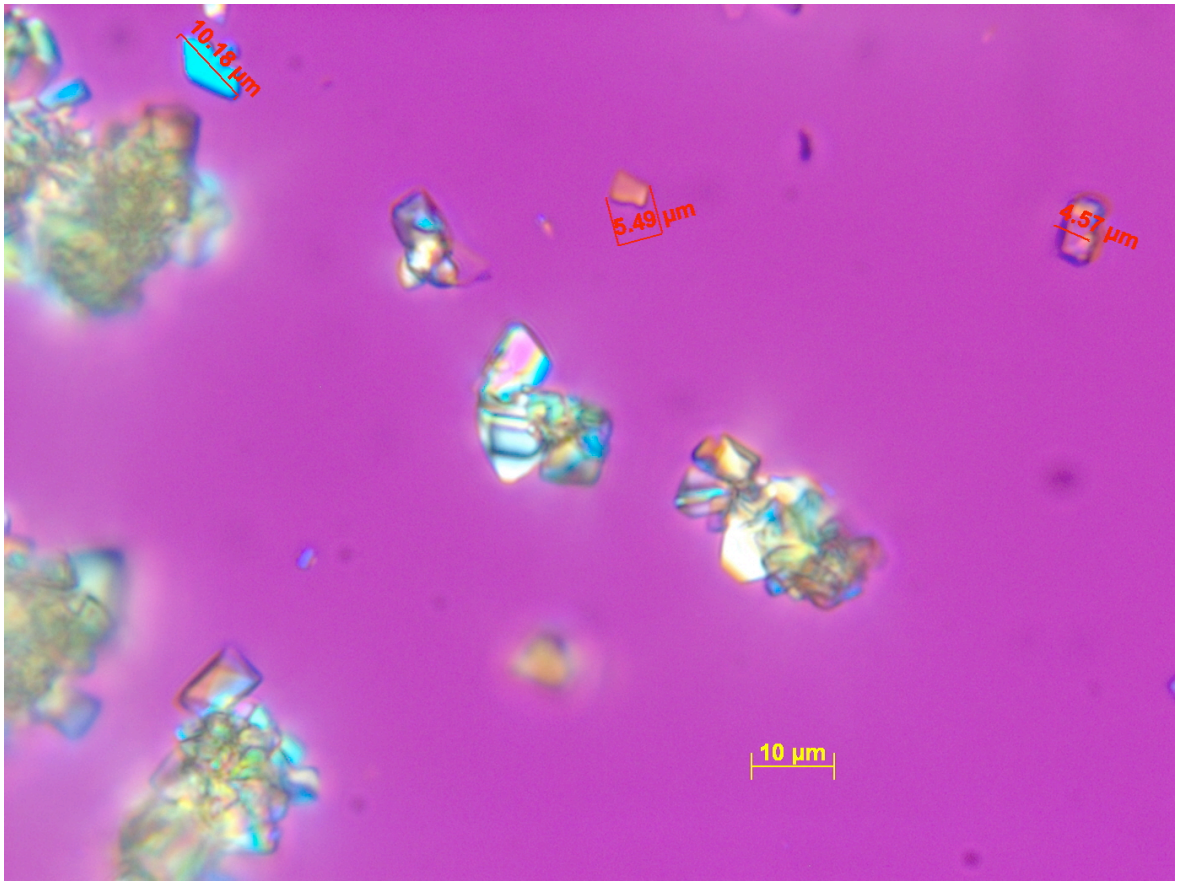

Figure10: Micrograph of CP lot EL-82936.

Even with these uncertainties, lot EL-82936 of CP compares fairly well to other known CP material. In making this assessment, it became obvious that existing data should be compiled in a more accessible format. Also, future plans should consider bringing all laboratories that have a need for understanding the stability of CP together to discuss unification of testing methods. This will not only bring analyses and results in-line, but it will also insure that a better understanding of the stability of an energetic material such as CP is safe for all that are exposed to its handling, operation or use.

ACKNOWLEDGMENTS

We thank Mr. George Overturf and Dr. Mark Hoffman of LLNL for their technical discussions, help and support on this project. Aaron Fontes conducted the sensitivity test. This work performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory, under Contract number W-7405-Eng-48. UCRL-JRNL-216115

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